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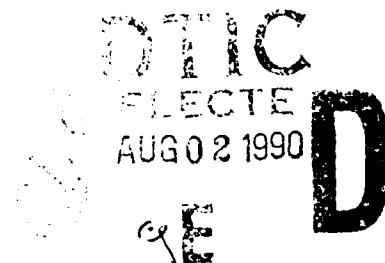
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Purification of Metal Fluorides for the Ultra  
Low Loss Program

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<p>By using radiotracer techniques the practical limits for the preparation of high purity ZrF<sub>4</sub>, HfF<sub>4</sub>, and LaF<sub>3</sub> via NRL current technology have been determined. The required concentration of impurities in BaF<sub>2</sub>, AlF<sub>3</sub>, and NaF for a 0.01 dB/km loss are calculated assuming the ZrF<sub>4</sub>, HfF<sub>4</sub>, and LaF<sub>3</sub> purification techniques are optimized to produce the impurity concentrations determined via radiotracer experiments.</p> <p>The significance of this work to the Ultra-Low Loss Program is: 1. The radiotracer study has shown that current NRL technology is capable of producing ZrF<sub>4</sub>, HfF<sub>4</sub>, and LaF<sub>3</sub> which contain low to sub-ppb concentrations of transition and rare earth element impurities. 2. The calculated impurity concentrations for BaF<sub>2</sub>, AlF<sub>3</sub>, and NaF define a realistic goal for new purification techniques. 3. The required impurity levels in BaF<sub>2</sub>, AlF<sub>3</sub>, and NaF are achievable via current technology. Radiotracer results indicate sub-ppb concentrations of impurities are achievable in ZrF<sub>4</sub>, HfF<sub>4</sub>, and LaF<sub>3</sub>, therefore, such levels should be possible in BaF<sub>2</sub>, AlF<sub>3</sub>, and NaF. This will be addressed in a future paper.</p>			
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# PURIFICATION OF METAL FLUORIDES FOR THE ULTRA LOW LOSS PROGRAM

## I. INTRODUCTION

In order to prepare a fluoride fiber exhibiting a loss of 0.01 dB/km the concentrations of the impurities Fe, Co, Ni, Cu, and Nd in the raw materials and the glass must be in the part-per trillion regime. A crucial question for the ultra low loss program's viability is whether materials of such high purity can be prepared and incorporated into a ZBLAN glass fiber? The purpose of this report is twofold; firstly determine where we are in purification technology with respect to our best purification techniques currently used for  $ZrF_4$  and  $LaF_3$  preparation, and secondly to determine the purity requirements for  $BaF_2$ ,  $AlF_3$ , and  $NaF$ . Radioactive tracer techniques are used to predict the minimum impurity concentrations in zirconium and lanthanum fluorides prepared via recrystallization and coprecipitation, respectively. Assuming the minimum impurity concentrations in zirconium and lanthanum fluorides are achievable in actual practice the impurity levels in these materials can be fixed. Using this data the impurity concentrations in the other metal fluorides,  $BaF_2$ ,  $AlF_3$ , and  $NaF$  are calculated.

The processes of recrystallization ( $ZrF_4$ ,  $HfF_4$ ), coprecipitation ( $La(NO_3)_3$ ), and hydrofluorination ( $ZrF_4$ ,  $HfF_4$ ,  $LaF_3$ ) have been studied experimentally by addition of radioactive tracers into key stages in the processing of these materials and following the distribution of the radioactive tracer as the purification process is carried out. In the present work, the radioactive tracers  $^{59}Fe$ ,  $^{60}Co$ ,  $^{88}Y$ , and  $^{139}Ce$  are added to the reaction media and the solution homogenized usually by stirring until the radioactive tracers are uniformly distributed throughout the solution. At this point it is assumed that the radioactive tracers cannot be chemically distinguished from their non-radioactive counterpart initially present in the raw material. Chemical processing is then carried out on the spiked solution and representative samples of the reaction products are taken. The distribution of the radioactive tracers between the two phases (in this case solid and liquid) is measured and expressed as a fraction of the total radioactive spike added, called the "spike fraction." The distribution of impurities after a single purification step on an unspiked sample is calculated by multiplication of the spike fraction by the known impurity concentration in an unspiked sample.

Using this data we can calculate the purification limits for the processes of recrystallization, coprecipitation and hydrofluorination. Once determined, these minimum impurity concentrations in  $ZrF_4$  and  $LaF_3$  can be used to calculate the impurity concentrations in  $BaF_2$ ,  $AlF_3$ , and  $NaF$  required to achieve a loss of 0.01 dB/km. This step is significant in that for the first time we can use experimentally determined impurity concentrations on the sub-ppb order (via radiotracer) to fix the absorption contribution of two of the five components of ZBLAN glass.

## III. EXPERIMENTAL

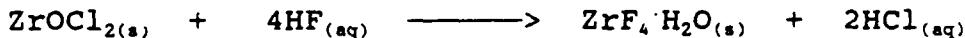
### A. ZIRCONIUM/HAFNIUM FLUORIDE PURIFICATION TECHNIQUE.

1. Use high purity zirconium tetrachloride to prepare zirconium oxychloride.



The resulting zirconium oxychloride solution is then filtered through a 0.2  $\mu\text{m}$  filter to remove particulates.

2. The filtered zirconium oxychloride solution is added to a 38% solution of HCl causing the zirconium oxychloride to recrystallize over a period of several hours.
3. The recrystallized zirconium oxychloride is then washed, pulped, and soaked with 7N HCl. The purified zirconium oxychloride is recovered by vacuum filtration. The recrystallization process is then repeated on the purified zirconium oxychloride.
4. Aqueous HF is then added directly to the recrystallized solid zirconium oxychloride. The solid dissolves rapidly and within 5 minutes a fine precipitate of zirconium fluoride monohydrate begins to form.



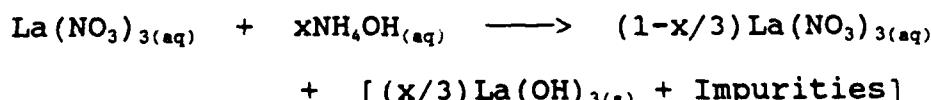
The precipitate is allowed to age for 20 hours; it is then recovered via vacuum filtration. The purified zirconium or hafnium monohydrate is then dried in an oven at 110°C for 2 hours.

### B. LANTHANUM FLUORIDE PURIFICATION TECHNIQUE

1. Use high purity lanthanum oxide with [Nd] = 7ppb. Purified via ion exchange at Ames Laboratory, Materials Preparation Center, Ames, Iowa.
2. Convert lanthanum oxide to lanthanum nitrate:

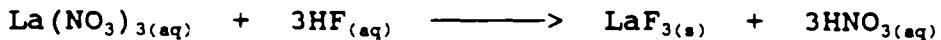


3. Add a small amount of concentrated ammonium hydroxide to the lanthanum nitrate solution prepared.



- D. The purified lanthanum nitrate is then converted to

lanthanum fluoride via addition of high purity hydrofluoric acid.



### III. Results and Discussion

#### 1. Zirconium and Hafnium Fluoride Purification

The results of the radiotracer study for the recrystallization of zirconium oxychloride and its subsequent conversion into zirconium fluoride monohydrate are given in Table 1. The initial impurity concentrations in the zirconium oxychloride are from analysis of material purchased from Teledyne, Wah Chang. The impurity concentrations in the hydrofluoric acid were determined via Isotope Dilution - Inductively Coupled Plasma - Mass Spectrometry (ID-ICP-MS) at the National Institute of Standards and Technology (NIST). The overall results can be summarized as follows:

1. Two recrystallization steps of zirconium oxychloride reduce:
  - a. Co, Ni, Cu, and Nd levels to sub ppb levels.
  - b. Fe to below 5 ppb.
2. Hydrofluorination of the recrystallized zirconium oxychloride:
  - a. Reduces all impurities to sub-ppb levels.
3. Loss contributed to the glass due to impurities, assuming  $\text{Fe}^{3+}/\text{Fe}^{2+} = 50$ , in zirconium fluoride is:

$$\underline{0.0016 \text{ dB/km}}$$

\*Paulson, P.J.; Beary, E.S.; Bushee, D.S.; Moody, J.R. Anal. Chem. (1988) 60, 971-975. Analysis via Isotope Dilution Inductively Coupled Plasma - Mass Spectrometry.

#### 2. Lanthanum Fluoride Purification

The results of the radiotracer study for purification via coprecipitation of lanthanum nitrate and its subsequent conversion into lanthanum fluoride are given in Table 2. The initial values for impurity concentrations in the lanthanum nitrate are of lanthanum oxide obtained from Ames Laboratory, Materials

Preparation Center, Iowa State University, Ames, Iowa. As in the case for zirconium fluoride purification NIST hydrofluoric acid impurity concentrations are used. The overall results can be summarized as follows:

1. Coprecipitation of a lanthanum nitrate solution:
  - a. Reduces the concentration of Co and Ni to below 10 ppb.
  - b. Reduces the concentration of Fe, Cu, and Nd to sub-ppb levels.
    - o Initial [Nd] = 7 ppb via ion exchange at Ames Laboratory, Iowa State University.
2. Hydrofluorination of the  $\text{La}(\text{NO}_3)_3$  solution incorporates the following amount of each impurity into the final fluoride:
  - o 100% Fe, Ni, Cu, and Nd present in  $\text{La}(\text{NO}_3)_3$  and HF solutions.
  - o 60% Co present in  $\text{La}(\text{NO}_3)_3$  and HF solutions.
3. Loss contributed to the glass, assuming  $\text{Fe}^{3+}/\text{Fe}^{2+} = 50$ , due to impurities in lanthanum fluoride is:

$$\underline{0.0014 \text{ dB/km}}$$

3. Maximum Concentration of Impurities in Barium, Aluminum, and Sodium Fluorides

Using the radiotracer derived impurity concentrations for  $\text{ZrF}_4$  and  $\text{LaF}_3$  as real numbers the impurity concentrations in  $\text{BaF}_2$ ,  $\text{AlF}_3$ , and  $\text{NaF}$  can be calculated for a fluoride fiber with 0.01 dB/km loss. The results of this calculation are given in Table 3 and the current analysis of NRL best materials are given in Table 4. The results in Table 3 were calculated using LOTUS software by varying the impurity concentrations in  $\text{BaF}_2$ ,  $\text{AlF}_3$ , and  $\text{NaF}$  until the loss is approximately 0.01 dB/km. The results are not unique solutions and are interdependent, for example, if the neodymium concentration in  $\text{BaF}_2$  is an order of magnitude lower than shown more neodymium could be tolerated in sodium fluoride. All materials in Table 4 were analyzed at NRL via Graphite Furnace Atomic Absorption Spectrometry (GFAAS) with the exception of aluminum fluoride which was analyzed via Spark Source Mass Spectrometry (SSMS). Results of the calculation can be summarized as follows:

1. The required impurity concentrations in these three materials are in the range; 0.3 - 1.0 ppb (ng/g).
  - o This gives a realistic target for evaluation of purification techniques.
2. Fe is at least an order of magnitude too high in BaF<sub>2</sub> and AlF<sub>3</sub>.
3. Cannot make any statement about the concentrations of impurities below instrumental detection limits.
  - o Currently working in improvement of detection limits.

#### IV. CONCLUSIONS:

This study has shown:

##### ZrF<sub>4</sub>/HfF<sub>4</sub>

1. Using available HCl and HF zirconium fluoride can be prepared with sub-ppb levels of impurities. This translates into a loss in the fiber due to impurities carried by ZrF<sub>4</sub> of:

0.0016 dB/km.

##### LaF<sub>3</sub>

1. Coprecipitation removes impurities in the order:

Fe>>Cu>Nd>Ni>Co

2. Using available HF and La(NO<sub>3</sub>)<sub>3</sub>, purified via coprecipitation, LaF<sub>3</sub> can be prepared with Ni levels below 10 ppb and Fe, Co, Cu, and Nd at sub-ppb levels.
  - o Initial material must first be purified via ion exchange to remove Nd.
  - o La(NO<sub>3</sub>)<sub>3(aq)</sub> + 3HF<sub>(aq)</sub> —> LaF<sub>3(s)</sub> incorporation of oxide is a problem

3. The loss in the fiber due to impurities carried by LaF<sub>3</sub> is:

0.0014 dB/km.

Maximum Impurity Concentrations in BaF<sub>2</sub>, AlF<sub>3</sub>, and NaF.

1. Required purification range 0.3 - 1.0 ppb
  - o BaF<sub>2</sub>, AlF<sub>3</sub>, and NaF
2. Fe very high in BaF<sub>2</sub> and AlF<sub>3</sub>
3. Analytical development is required to lower detection limits for impurities.

TABLE I  
ZIRCONIUM FLUORIDE PURIFICATION  
 RADIOTRACER STUDY

CONCENTRATION, PPB					
<u>COMPOUND</u>	<u>Fe</u>	<u>Co</u>	<u>Cu</u>	<u>Ni</u>	<u>Nd</u>
ZrOCl <sub>2</sub>	310	50	10	50	10
1 RECRYST.	16	3	0.5	3	0.5
2 RECRYST.	2	0.4	0.07	0.4	0.07
HF <sub>(aq)</sub>	0.6	0.001	0.035	0.53	0.0003
ZrF <sub>4</sub> ·H <sub>2</sub> O	0.27	0.05	0.012	0.09	0.068
LOSS (dB/Km)	5E-05	5E-04	2E-05	1E-04	9E-04
TOTAL LOSS (dB/Km) = 0.0016 dB/Km					
[Fe <sup>3+</sup> /Fe <sup>2+</sup> = 50]					

TABLE 2  
LANTHANUM FLUORIDE PURIFICATION  
 RADIOTRACER STUDY

		Concentration, ppb				
		<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Nd</u>
La(NO <sub>3</sub> ) <sub>3</sub>	Initial	1165	6	24	27	7
1 Coppt.		63	4	15	2	1.6
2 Coppt.		3.5	2.9	9.8	0.17	0.36
3 Coppt.		0.19	2	6.3	0.01	0.08
4 Coppt.		0.01	1.4	4	0.001	0.02

o Use Lanthanum Nitrate from Fourth Coprecipitation Step

	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Nd</u>
La(NO <sub>3</sub> ) <sub>3</sub>	0.01	1.4	4	0.001	0.02
HF <sub>(aq)</sub>	0.6	0.001	0.53	0.035	0.0003
LaF <sub>3</sub>	0.61	0.82	4.53	0.036	0.0203

Contribution, dB/km

<u>Impurity</u>	<u>Loss Contribution, dB/km</u>
Fe	1.0E-05
Co	7.7E-04
Ni	5.9E-04
Cu	5.9E-06
Nd	2.5E-05

Total loss contributed by LaF<sub>3</sub> in glass = 1.4E-03 dB/km

o Assuming Fe<sup>3+</sup>/Fe<sup>2+</sup> = 50

Table 3

Maximum Concentration of Impurities

In ZBLAN Components for 0.01 dB/km Loss

Concentration, ppb

	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Nd</u>
ZrF <sub>4</sub> <sup>+</sup>	0.27	0.05	0.09	0.012	0.068
BaF <sub>2</sub>	1.0	0.5	0.5	0.5	0.3
LaF <sub>3</sub> <sup>+</sup>	0.61	0.82	4.5	0.036	0.02
AlF <sub>3</sub>	1.0	1.0	1.0	1.0	0.6
NaF	1.0	1.0	0.9	0.9	0.5

<sup>+</sup>Impurity concentrations achievable by current techniques as determined by radiotracer study.

TABLE 4  
NRL BEST MATERIALS

	Concentration, ppb				
	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Nd</u>
ZrF <sub>4</sub>	<10	<10	<10	<10	<0.05
BaF <sub>2</sub>	70	<21	<93	<9	unk.
LaF <sub>3</sub>	<81	<32	<98	<73	7
AlF <sub>3</sub>	60	<20	<30	<30	unk.
NaF	<49	<49	<74	<20	unk.

NOTE: The symbol < denotes that the impurity concentration is below the instrumental detection limit. All metal fluorides are analyzed by GFAAS except for AlF<sub>3</sub>, which is analyzed by SSMS.

GFAAS - Graphite Furnace Atomic Absorption Spectrometry

SSMS - Spark Source Mass Spectrometry